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Homogenization Study of Molybdenum and Copper in P/M Steel

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ABSTRACT

Homogenization of 3wt% Molybdenum addition in Fe-0.7C alloy in the presence of 2wt% Cu under sinter-forged condition has been carried out. Samples alloys have been fabricated by sinter-forging route using elemental powders. Sintering was carried out at 1150oC in N2-10%H2 atmosphere. The sintered samples were immediately forged using 100-ton friction screw forging press at the sintering temperature. Homogenization studies were carried out in two steps, the preliminary study was carried out on a press-sinter-forged compact while the final study was carried out on sinter-forged slab prepared by capsule forging. Homogenization temperature was kept at 1250oC (heating rate of 10oC / min) in flowing N2-10%H2 atmosphere for various durations between 1-5 hr. The extent of Mo and Cu dissolution in the Fe matrix of homogenized samples was ascertained using microstructural characterization under optical microscope, SEM and EDS analysis. The influence of initial powder particle size, sintering temperature and homogenization temperature & duration on homogenization behavior have been discussed in length.

Keywords: Fe-C P/M alloys; Sinter-forging; Molybdenum; Copper; Homogenization; Microstructure.

INTRODUCTION

Homogeneous distribution of the alloying elements is essential while using elemental powders in order to obtain uniform and consistent properties of P/M products (Danninger, 1987, Torralba et. al., 1992 & Danninger 1987 et. al. 2007). Uniform and faster homogenization can be achieved by formation of liquid phase by melting of alloying element at the sintering temperature like Fe-Cu-C, Fe-P, W-Ni-Fe, etc. (Das et. al., 2012 & Rathore et. al., 2013) alloys. Fe-Cu-C (Iron-Copper-Carbon) alloy is widely employed for production of structural parts and automotive applications (Arbstedt, 1976, German, 1998, Amador et. al., 2003 & Engstrom, 2003). However, with elemental Mo due to its much higher melting point than that of the matrix (Fe-C) (Engstrom et. al. 2001) and very slow distribution of Mo by solid state diffusion (Heckel, 1978), liquid phase sintering is not possible. Further, Cu and Mo show a miscibility gap (Subramanian et. al., 1990). Homogenization of elemental Mo in Fe-C system has been reported by Danninger H. It has been reported that by interdiffusion of the components transient liquid phase is generated in Fe-Mo-C system at temperature more than 1200oC between η- carbide and austenite by forming eutectic. Formation of ternary eutectic (Fe-13Mo-3.7C) mainly contributes to the homogenization of elemental Mo (Danninger, 1988 a) which influences on the carbon content, Mo powder particle size, matrix density and sintering temperature (Danninger, 1988 b).

Mo in P/M steels may be added in form of pure elemental, partially or fully prealloyed and diffusion bonded powders (Danninger, 1992, Bocchini et. al., 2004, Yilmaz et. al., 2007, Huang et. al., 2011, Ghandi et. al., 2016 & Erden et. al., 2021). Usually, with prealloyed powders excellent homogeneity of alloying elements can be achieved but these powders have problems of compressibility. However, Mo prealloyed powder does not suffer from compressibility problem due to high compressibility of Mo. On the other hand, elemental powders provide better compactibility,

compositional flexibility and they have easy availability with comparatively less cost (Cambronero et. al., 1994). In addition to type of powder form, initial particle size of the powder and sintering temperature also influence homogenization of alloying elements and properties of the P/M alloys (Danninger, 1988, Smith et. al., 1977 & Candela et. al., 2005). Diffusion bonded powders eliminate segregation problem. Chen et al., 2018 have investigated addition of different pure Mo powder, prealloyed Mo-Fe powder and mechanically alloyed Mo- Fe powder in Fe-2Cu-0.8C using warm compacted sintered alloys and reported sintered samples prepared with mechanically alloyed Fe-Mo powders exhibited better microstructure and mechanical & wear properties (Chen et. al., 2019). Effect of particle size distribution of iron based pre-alloyed Fe-2Cr-0.2Mo with addition of 0.25%C was investigated by Jung G. Lee et al. using magnetic pulsed compaction and 7.75 g/cm3 sintered density was achieved (Lee et. al., 2012). Büyükkayacı et al. 2020, reported that microstructure of Fe-Cu-C P/M alloys and its wear behaviour is greatly influenced by mechanical alloying time (Buyukkayacu et. al., 2020). Trivedi S et al., have reported to achieve 98.9% of the theoretical density using hot powder forging technique of Fe–0.45P and Fe–0.45P–3Cr alloys with elemental powders (Trivedi et. al., 2010). Based on the literature, an attempt is made to investigate the homogenization behaviour of Ferro Mo powder in the presence of 2wt%Cu and 0.7wt%C in the sinter-forged (high density) condition and influence of particle size, homogenization temperature and time thereon in this study.

MATERIALS AND METHOD

In this study, water-atomized elemental iron powder (HoganasTM India- ASC.100.29, 99.9% purity) and elemental electrolytic Cu powder (HimediaTM India, minimum purity 99.7%) were used while carbon was added in form of natural graphite. Molybdenum was added in form of ferro-molybdenum powder (KammanTM India). Particle size distribution of Fe, Cu, Fe-Mo and graphite powders was determined using a particle size analyzer (ANKERSMID CIS-100 computerized inspection system). The powder morphology was observed under SEM (ZEISS SUPRA 55VPTM) while the powder phases were determined by X-ray diffraction (XRD) technique using Expert High Score PlusTM software. Homogenization studies were carried out in two steps; preliminary study was carried out on a press-sinter-forged compact while the final study which was carried out on sinter-forged slab prepared by capsule forging.

Preliminary study (press-sinter-forged compact): For preparing press-sinter-forged compact of Fe-2Cu-0.7C-3 Mo composition the powders were weighed carefully using an electronic balance. The total weight of powders used for one compact was 100 gm. The mixing of powders was carried out in a planetary mill (Retch PM 400/2 TM) under dry condition. The ball mill was run at 160 rpm for 15 minutes and powder to ball ratio was used at 1:5. The powder mix was then pressed uniaxially in a 50T hydraulic press. A 500 MPa compaction pressure was applied to produce a green compact of 48 X 22 X 17 mm average size using floating die. The die walls were lubricated with a mixture of acetone and sodium silicate to ensure easy ejection of the compact and to prevent powder from sticking to its surface. The green compact was sintered at a temperature of 1120oC in reducing atmosphere of N2-20% H2 for 40 minutes in a tubular furnace. The sintered compact was immediately hot forged using 100T manually operated Weingarten-type (make BIRSONTM, Ludhiana, India) screw friction forging press at the sintering temperature (1120oC) followed by air cooling. The forged compact was homogenized at 1300oC in N2-20% H2 atmosphere for two hours for dissolution of ferro-molybdenum in the matrix. Density was measured by Archimedes method. Microstructural samples were prepared from homogenized compact and observed under optical microscope and SEM.

Final study (sinter-forged slab): To facilitate homogenization of ferro-molybdenum powder in final homogenization study modifications have been incorporated (a) the average particle size of 45 μm of Fe-Mo powder was reduced to less than 10 μm size, (b) the sintering temperature was increased from 1120oC to 1150oC. The particle reduction of Fe-Mo powder was carried out by wet milling (in toluene) in a planetary ball mill (Retch PM 400/2 TM) for various durations between 1- 3 hr at a speed of 200 rpm. The hardened steel balls of bearing grade of different diameters were used with a charge to ball ratio of 1:10. After every one hour of milling, milled powder sample were collected and were observed under SEM to measure its particle size Therefore, it was decided to mill Fe-Mo powder to 3 hr to ensure a particle size of less than 10 μm. According to the composition, individual powders were carefully weighed in an electronic balance and the powder blend was first manually mixed in a mortar pestle for 20 minutes and then in a double cone mixer for 60 minutes. In this way a powder blend of approximately 1 Kg was prepared which was then filled

into a mild steel capsule. Sintering was carried out at a temperature of 1150oC with heating rate of 10oC / min and holding time of 40 min in a flowing reducing atmosphere of N2-10% H2. The sintered capsules after holding for 40 min at the sintering temperature were quickly transferred to a channel die of dimensions (22 x 7 x 2.5 cm) fitted over a manually operated forging friction screw press of 100-ton capacity to obtain forged slabs. From the Fe-2Cu-0.7C-3Mo forged slab rectangular samples were cut at a location near to end caps and homogenized in the same tubular furnace used for sintering. The tube furnace was first evacuated using a rotary pump after which it was filled with N2-10% H2 gas which was allowed to flow during the homogenization period. Homogenization was carried out at 1250oC (heating rate of 10oC/ min) for various durations between 1-5 hr. After every one hour of homogenization, samples were taken out for microstructural characterization to study the homogenization of alloying elements under optical microscope and SEM.

RESULTS AND DISCUSSION

Powder Characterization

The SEM images exhibiting morphology of copper, iron and ferro-molybdenum powders are shown in Figure 1 (a-c) respectively. SEM images exhibited dendritic morphology of Cu powder (Figure 1(a)) and irregular morphology for both iron and ferro-molybdenum powders (Figure 1 (b-c)).

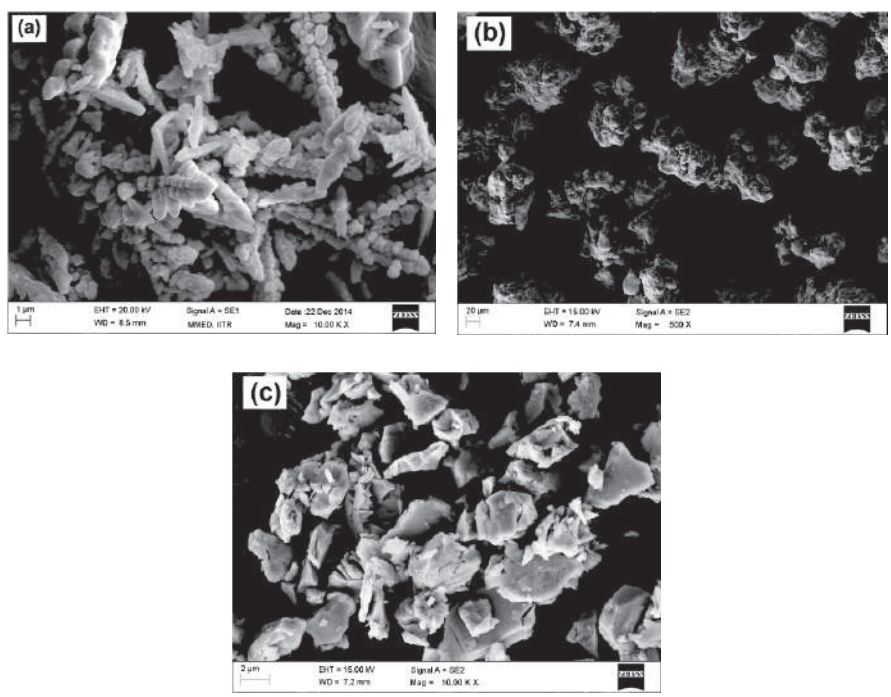


Figure 1. SEM micrographs of powders (a) Cu (b) Fe and (c) Fe-Mo (3 hr milled)

Physical properties of various powders used in the present work have been determined and are shown in the Table 1.

Table 1. Physical properties of various powders used

Powder	Apparent Density (g/cm^3)	Tap Density (g/cm^3)	Flow Rate (s/50g)
Fe	3.1 (39% of TD)	4.3 (54% of TD)	24
Fe-Mo	4.58 (42% of TD)	5.69 (52% of TD)	22
Cu	2.2 (22% of TD)	2.8 (31% of TD)	Non-free flowing

The X-ray diffraction (XRD) pattern of Cu powder, Fe powder and Fe-Mo powder are shown in Figure 2 (a-c). All peaks corresponding to Cu (FCC) were observed in the diffraction pattern of copper (Figure 2 (a)). Since the copper was of electrolytic grade it was of high purity did not exhibiting any other oxide or impurity peaks. Further, copper has less affinity for oxygen and these powders do not readily oxidize at room temperature. The diffraction pattern of Fe powder also exhibited all peaks corresponding to ferrite (B.C.C). These powders were synthesized by reduction and do not contain any oxide in the synthesized state. Iron has good affinity for oxygen and the powders are likely to form the oxide layer over time. But this was not detectable in the XRD as a volume fraction of more than 5-7% is required for detectability. The ferro-molybdenum (Fe-Mo) powder showed all peaks corresponding to Fe3Mo. As in the case of Fe powder no oxide peaks were visible in the Fe-Mo powders

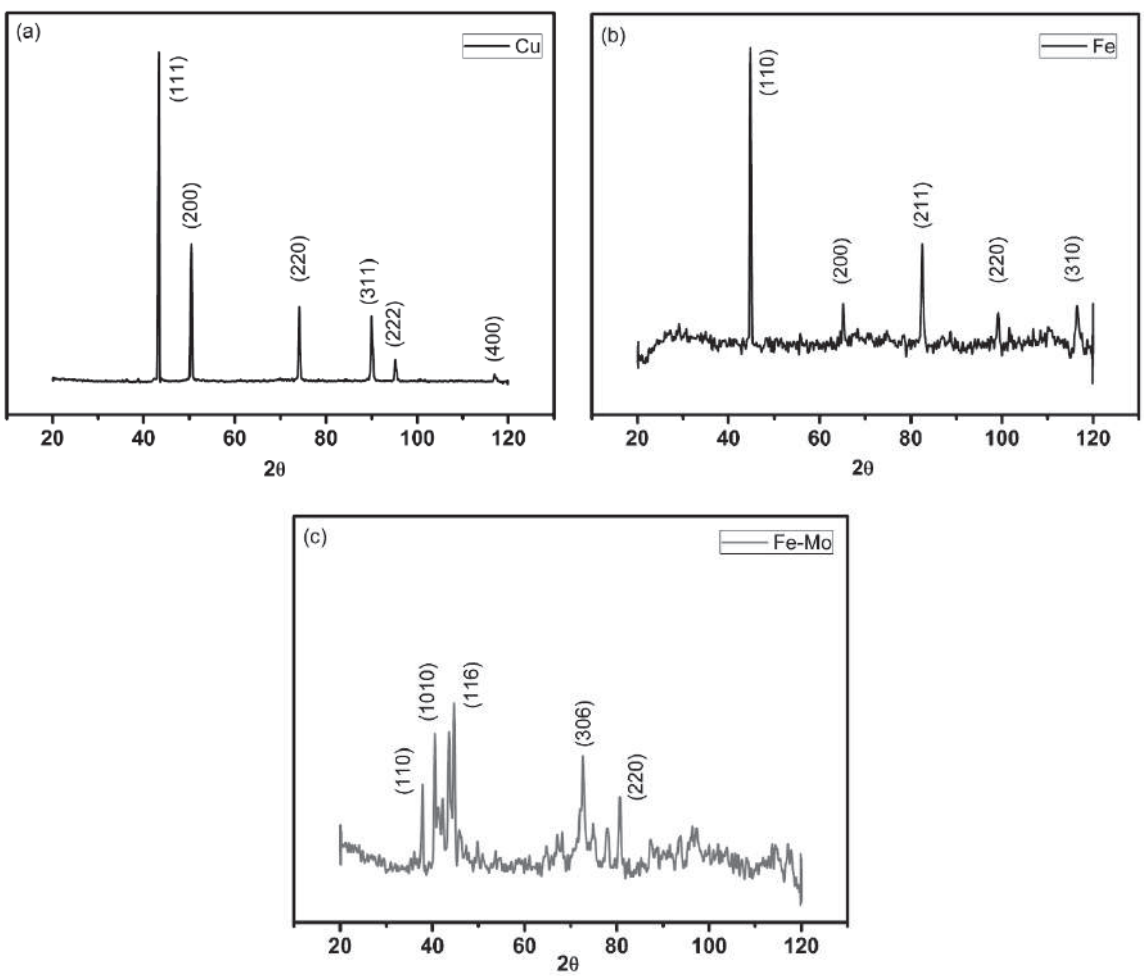


Figure 2. XRD pattern of powders (a) Cu, (b) Fe, and (c) Fe-Mo respectively

The particle size distribution results of different powders used are shown in Figure 3. The average particle size of Cu powder is indicated to be 14 μm while that of elemental iron powder is to be 45 μm as shown in Figure 3 (a & b) respectively. It was found that 2 hr milled powder particle size reduced to considerable smaller size (around 15 μm) compared to its initial size (45 μm). However, some particles bigger than 10 μm were also observed whereas, no particle of >10 μm size were observed in 3 hr milled powder and the average particle size of 4-8 μm was observed. Similarly, after 3 hr of milling particle size distribution of ferro-molybdenum indicated as < 10 μm is shown in Figure 3 (c) whereas the graphite particle size distribution is shown in Figure 3 (d).

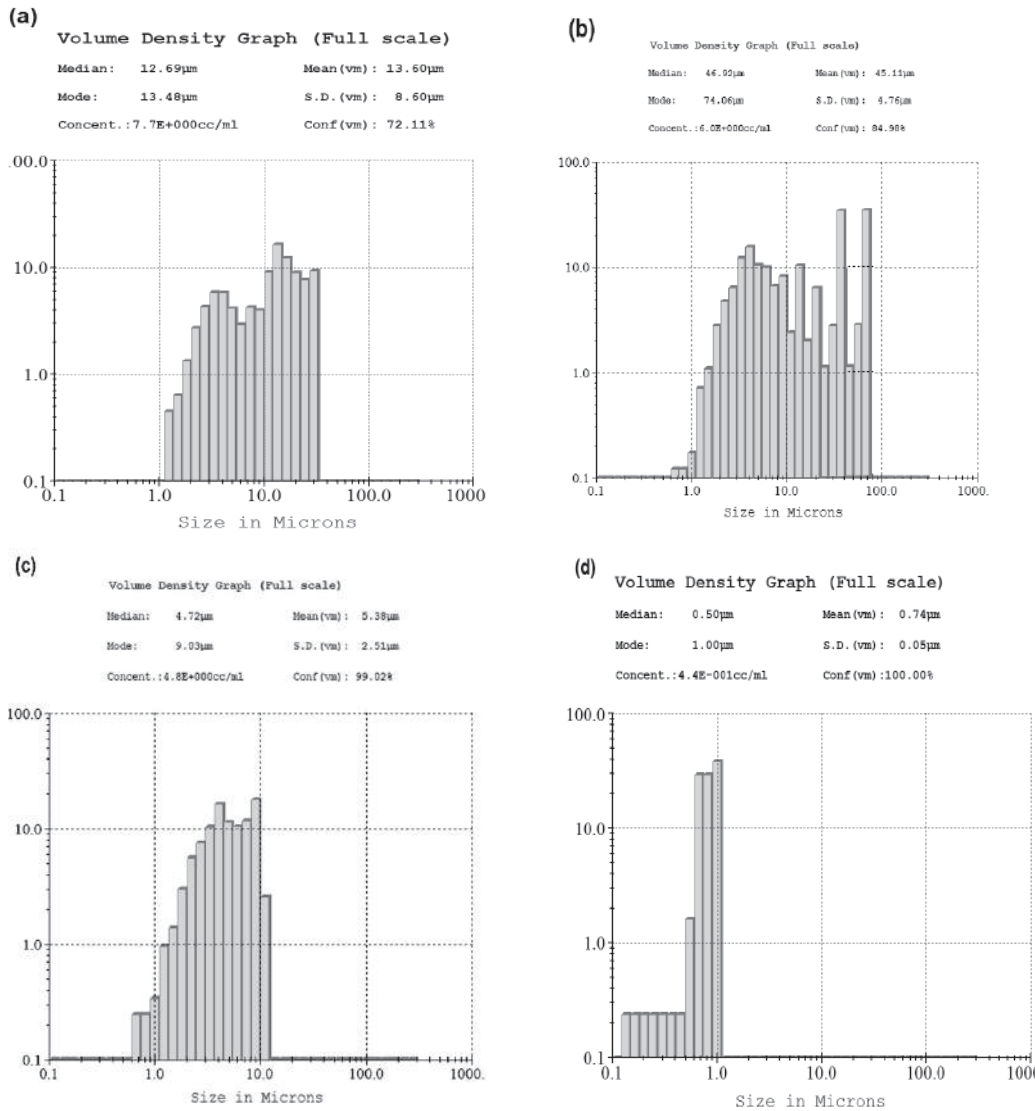


Figure 3. Particle size distribution (a) Cu, (b) Fe, (c) Fe-Mo (3 hr milled), and (d) Graphite powders respectively

HOMOGENIZATION STUDY

Preliminary study- press-sinter-forged compact

In the preliminary study as described earlier 45 μm average particle size of Fe-Mo powder was used and homogenization was carried out at 1300 oC for two hrs. The resultant microstructures of 3 wt% Mo are shown in the Figure 4.

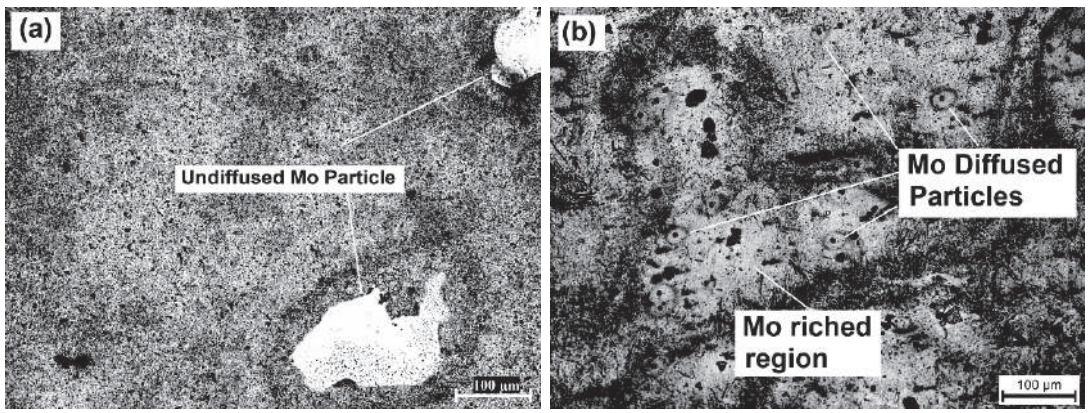


Figure 4. (a) Undiffuse /partially diffused Fe-Mo particles in 3wt% Mo Sinter-forged compacts, (b) Diffused Fe-Mo particles in 3wt% Mo Sinter-forged slab

In the microstructures some partially diffused/undiffused Fe-Mo particles were observed even after 2 hours of homogenization process at 1300oC (Figure 4 (a)). Though the average particle size of the Fe-Mo powder was 45 µm, it contained particle of larger and smaller sizes than the average particle size. It is clear that the smaller size particles (< 45 µm) could diffuse completely in the matrix during 2 hr of homogenization as a Mo gradient was observed in the microstructures. However, the larger size particles remained partially diffused during homogenization and these were still visible in the microstructure. But some disintegration of these larger size particles had started which is visible in the Figure 4. Presence of Fe-Mo particle was confirmed by EDS elemental analysis and the representative SEM image of Fe-Mo particle with EDS is shown in Figure 5. Figure 4 (a) shows martensitic zone and Mo rich region (white area) formed around the partially diffused Fe-Mo particle due to diffusion of Mo in Fe-C matrix by formation of transient liquid phase and solid-state diffusion processes.

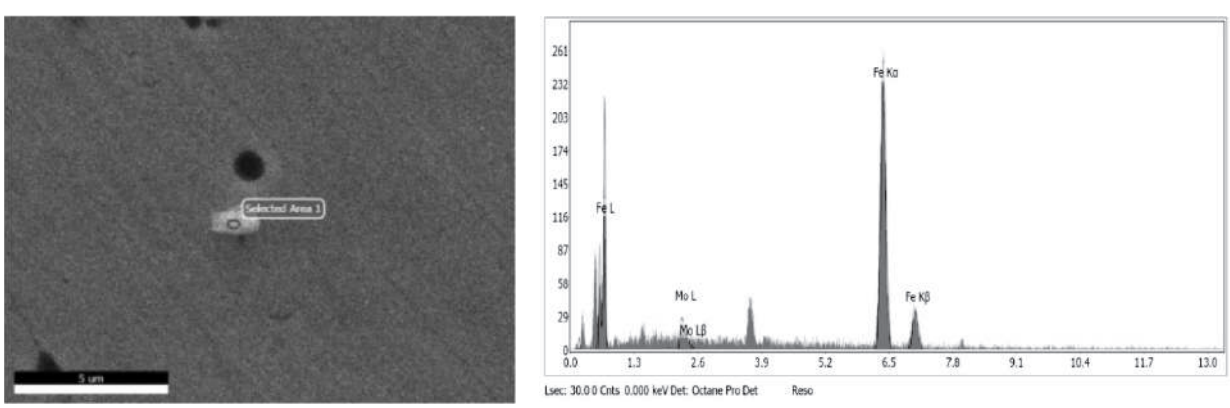


Figure 5. SEM image of Fe-Mo particle and corresponding EDS elemental result

The SEM image of the Fe-Mo-C eutectic formed during homogenization process with EDS results is shown in Figure 6. Both high density of the matrix and low carbon content, Mo (elemental) distribution by melt penetration in the matrix pores is inhibited (Danninger, 1988). In the present case as density of compact is 93% and carbon percentage is also moderate, this might cause limit compositional range of the melt for complete diffusion of Mo in liquid phase while solid state diffusion of Mo is reported as a very slow process. This may be the reason that incomplete diffusion of Fe-Mo particles was observed and two hours of homogenization was found to be insufficient with the initial average particle size of 45 μm of Mo used in this study.

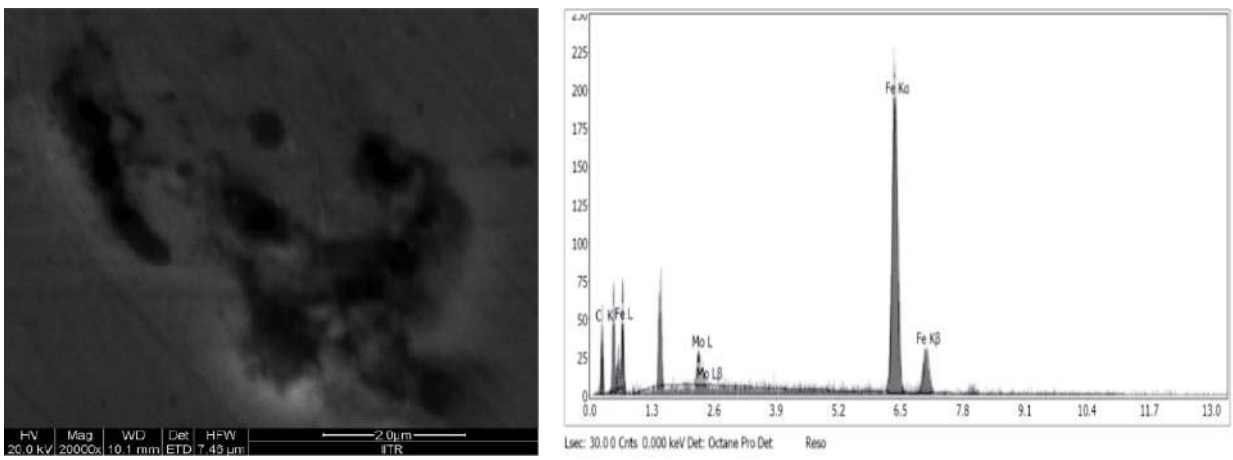


Figure 6. SEM image of ternary eutectic of Fe-Mo-C with EDS result

Final study- sinter-forged slab

Distribution of liquid phase in the Fe-C matrix is also influenced by the matrix density as well as the initial particle size of Mo where more homogeneous distribution of Mo is reported with fine powder (Danninger, 1988 b). The unetched micrograph of as reforged sample i.e. without any homogenization treatment (0 hr) showed some dissolution of Mo particle in the matrix (Figure 7a). The EDS analysis confirmed that the visible particles are of Fe-Mo powder. The EDS result along with corresponding SEM image is shown in Figure 7 (b). It is evident from the Figure 7(a) that in reforged condition now no large Fe-Mo particles were observed as that were observed prominently in the press-sinter and homogenized compacts as described earlier. However, some Fe-Mo particles in partially diffused state are visible. This indicates the beneficial effect of reducing initial particle size of Fe-Mo by milling. The SEM image exhibited some Mo particles (Figure 7(b)) with small ring formation (some dark grey area) around these particles which indicated the martensitic zone as described earlier. This ring represents Mo gradient in the matrix and indicates that the dissolution of Mo is in progress.

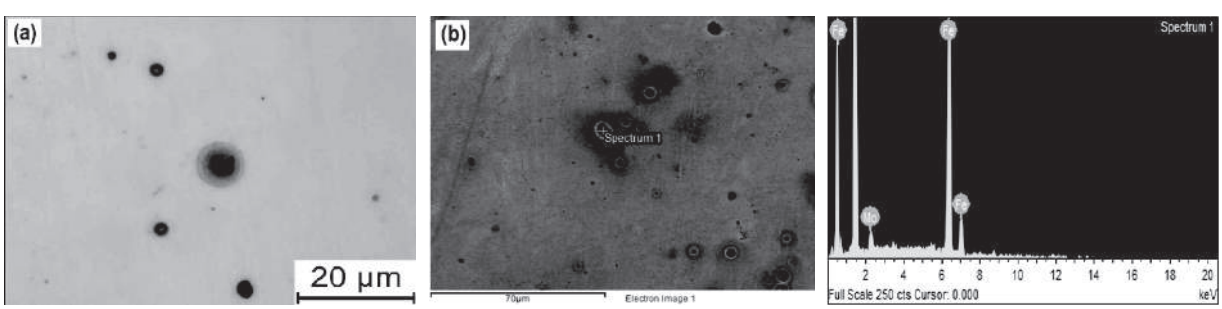


Figure 7. Fe-Mo particle in reforged condition (a) Optical micrograph and (b) SEM with EDS result

The distribution of Cu and Mo in reforged condition (0 hr) is better indicated in EDS dot map as shown in Figure 8 respectively. The EDS dot map revealed that diffusion of both Cu and Mo in the matrix has initiated. However, uniform homogenization of both was not achieved. The Cu concentration was found more at the boundary of the pores whereas the Mo was observed mainly at the surface of pores.

The status after 2 hours homogenization treatment is depicted in the optical micrograph shown in Figure 9 (a) where comparatively smaller size Fe-Mo particles were seen. The surrounding martensitic zone around the particles is visible which is comparatively light in colour and indicates that Mo is dispersing in the matrix and relatively some uniformity has been achieved in dissolution of Mo after two hours. The corresponding EDS map also supported the improved distribution of Mo as compared to 0 hr condition.

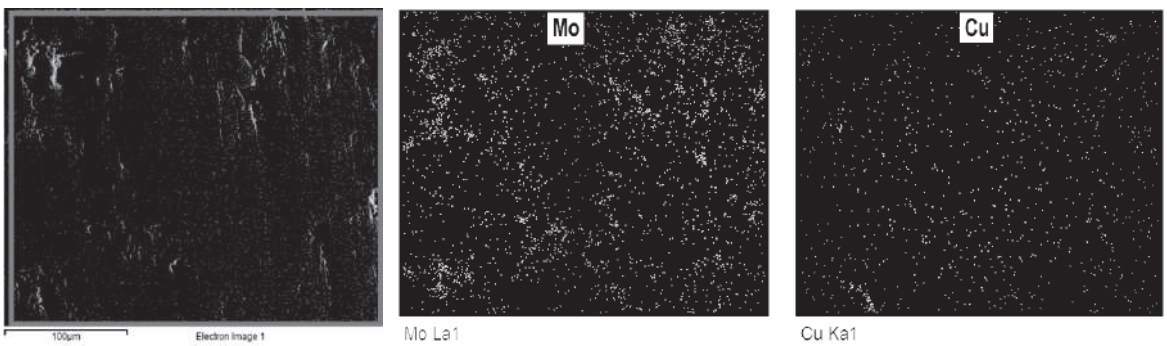
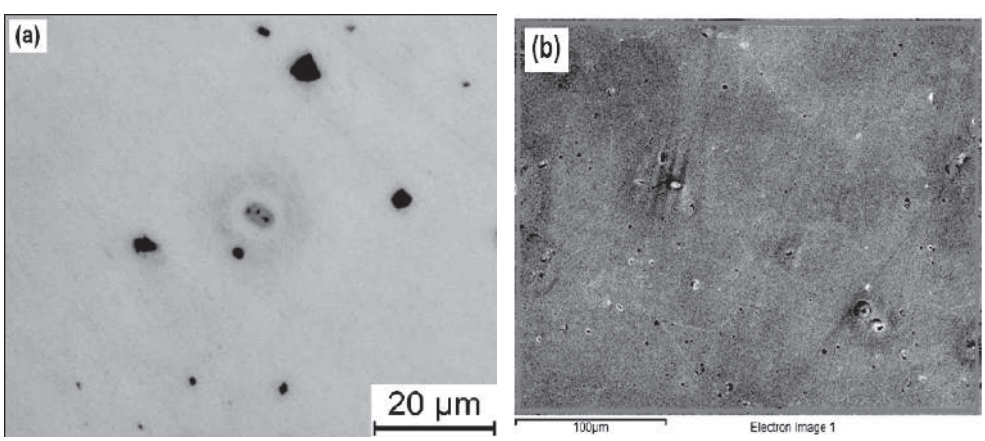


Figure 8. EDS dot map of Mo and Cu in sinter-forged condition

The distribution of elements after 2 hr homogenization as observed by EDS mapping are shown in Figure 9. The EDS map exhibited that Cu dispersed along the grain boundary whereas Mo has dispersed in the Fe-C grains. This is expected because due to greater affinity of C with Mo (Liu et. al. 2001), the dissolved C in Fe reacted with Mo and formed carbides as described by Danninger, 1988 and that helps in Mo dispersion in the Fe-C matrix. On the other hand, 2 hr was reported as sufficient time for Cu homogenization in Fe-Cu alloys sintered at 1150oC by Danninger, 1987. However, in present investigation it has observed that Cu homogenization was also affected by presence of both C and Mo. The already dissolved C in Fe reduced wettability of Cu and restricted Cu penetration in Fe. As a result, Cu was visible around the grain boundary.



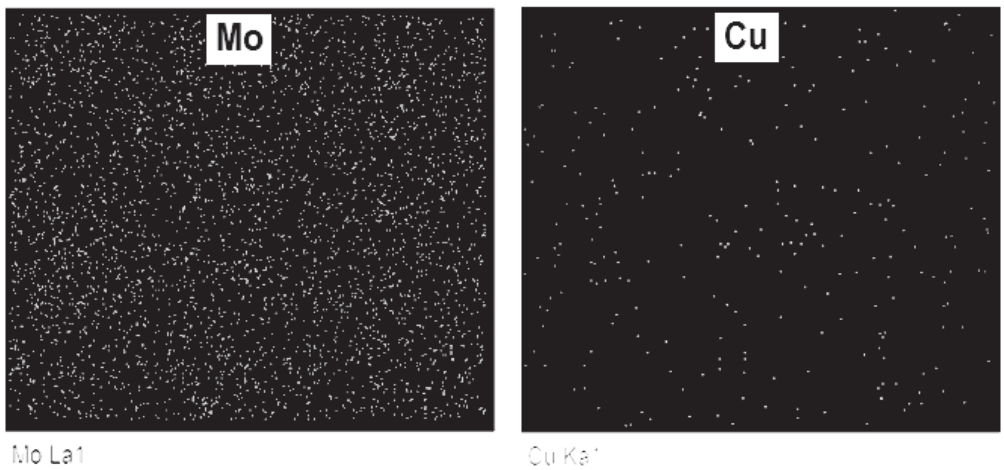


Figure 9. (a) Optical micrograph (b) SEM image with EDS mapping after 2 hr of homogenization After 4 hr of homogenization, much improved distribution of both Mo and Cu was achieved. The optical micrograph exhibited very small Fe-Mo particles and almost negligible gradient around it. The same situation was also exhibited in the SEM image and EDS map which confirmed that improved distribution of both Mo and Cu has been achieved. Cu which was mostly located along the grain boundary after 2 hr of homogenization has now uniformly dispersed in the matrix. After 5 hr of homogenization no Mo particle was visible in the optical micrographs and EDS dot map also demonstrated uniform distribution of both Mo and Cu as shown in in Figure 10. It indicated that almost complete homogenization of alloying elements has been achieved.

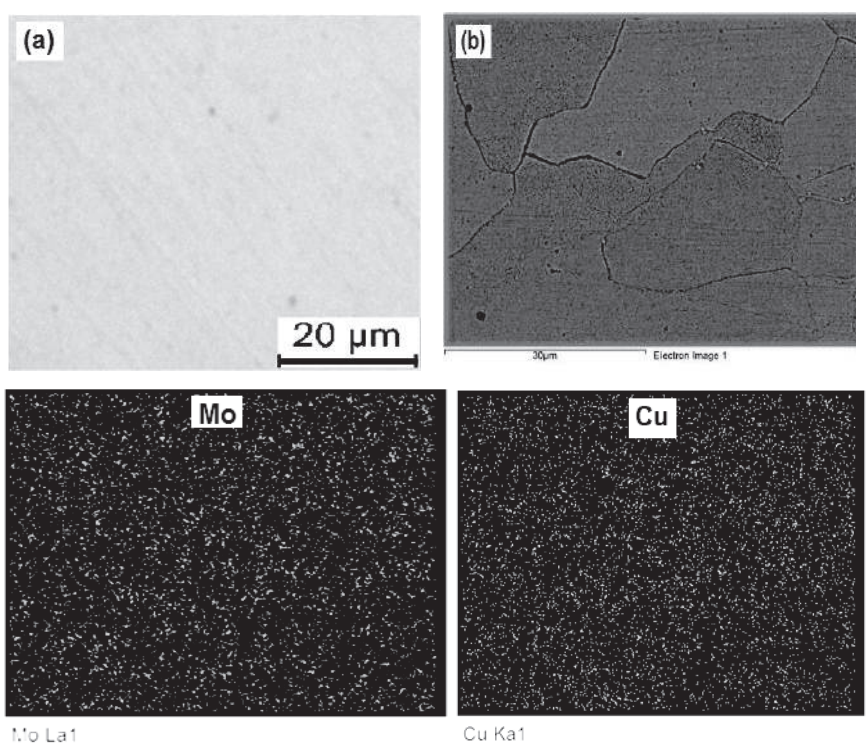


Figure 10. (a) Optical micrograph (b) SEM image with EDS mapping after 5 hr of homogenization

CONCLUSION

In the present experimental work demonstrates the homogenization of 3wt% Molybdenum in Fe-0.7C-2Cu alloy was successfully conducted using elemental powders and critically analyzed. Homogenization of elemental Fe-Mo influenced by the initial powder particle size, density level of matrix and presence of Cu. Complete homogenization of Fe-Mo with particle size < 10 μm could be achieved in 5 hr duration at 1250oC. It was found that using sinter-forging and reforging route, high density (>98%) Fe-2Cu-0.7C-3Mo could be achieved. The forged alloy exhibited a porosity level of < 1.27% with pores of diameters less than 3 μm that were isolated and rounded and therefore, may likely to be used for structural applications.

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